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(71) Applicant *(for all designated States except US)*: **AMCOR TWINPAK-NORTH AMERICA INC. ET AL.** [CA/CA]; 910 Central Parkway West, Mississauga, Ontario L5C 2V5 (CA).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **MULHOLLAND, Lindsay** [CA/CA]; RR #6, Cambridge, Ontario N1R 5S7 (CA). **GOODRICH, Nina** [CA/CA]; RR #6, Cambridge, Ontario N1R 5S7 (CA). **SENIOR, David** [CA/CA]; 275 Camborne Crescent, Burlington, Ontario L7N 2A4 (CA). **CHIU, Boris** [CA/CA]; 254 Brigadoon Drive, Hamilton, Ontario L9C 7S2 (CA).

(74) Agent: **STEWART, Michael, I.**; Sim & McBurney, 6th Floor, 330 University Avenue, Toronto, Ontario M5G 1R7 (CA).

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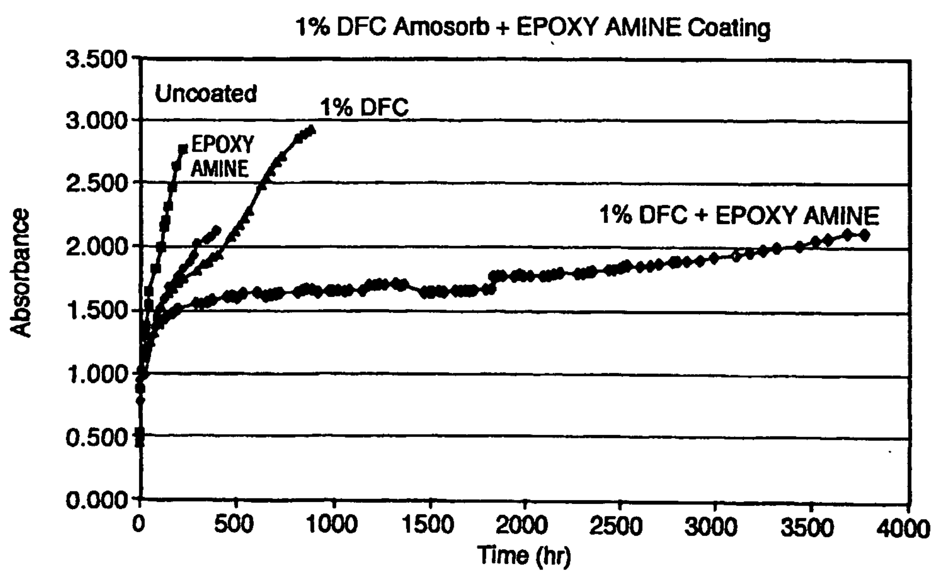
(54) Title: MODIFIED CONTAINER



(57) Abstract: The gas permeance of polyester bottles or other packaging article is improved by the combination of an oxygen scavenging material provided in the wall of the article and an external barrier to gas flow.

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TITLE OF INVENTION

MODIFIED CONTAINER

FIELD OF INVENTION

[0001] This invention relates to a packaging article, specifically a normally air-permeable container, which has been modified to reduce its gas permeability.

BACKGROUND TO THE INVENTION

[0002] Polyethylene-terephalate (PET) is widely used as the construction material for packaging articles for a variety of beverages, for example, juices, which may be carbonated, such as soft drinks and beer. PET is known to be permeable to gases, such as oxygen and carbon dioxide, which leads to a finite shelf-life to oxygen-sensitive products, such as juices and beer, packaged therein.

[0003] Attempts have been made to decrease the permeability of PET bottle walls by manipulation of the structure of the wall, to provide a shelf-life at least 2 to 3 times that of the unmodified bottle. One manner of manipulation of the structure of the wall is to incorporate substances capable of intercepting or scavenging oxygen as it attempts to pass through the walls of the container.

[0004] One method for use of such active absorbent is a sandwich arrangement in which the gas scavenging material is provided as an inner layer while the outer layers are formed of PET or other polyester packaging material. Alternatively, the gas scavenging material may be uniformly distributed in the wall structure.

[0005] A variety of materials has been suggested for use as the gas scavenging material, including poly(1,2-butadiene), as described, for example, in USP 5,310,497, polyamide, as described, for example, in USP 5,639,815, and condensation polymers comprising predominantly polyester segments and an oxygen scavenging amount of polyolefin oligomer segments, such as unhydrogenated polybutadiene, as described, for example, in USP 6,083,585.

[0006] Such scavenging materials tend to be expensive. The gas scavenging material eventually becomes exhausted of the ability to absorb oxygen, which leads to concerns with respect to empty bottle life.

SUMMARY OF INVENTION

[0007] It has now surprisingly been found that the oxygen transmission rate and capacity of the gas scavenging material may be greatly improved by applying an external passive barrier to gas flow both from exterior of the bottle and from interior of the bottle to at least the walls of the container.

[0008] Accordingly, in one aspect of the present invention, there is provided a packaging article having at least a wall constructed of a polyester and having an oxygen scavenging material therein and having an external barrier to gas flow therein. Since the oxygen barrier performance of the wall is improved, the quantity of active oxygen scavenger material can be significantly reduced while, at the same time, achieving an improved shelf-life.

BRIEF DESCRIPTION OF DRAWINGS

[0009] Figures 1 to 5 are graphical representative of data generated with respect to oxygen permeability, as described in detail in the Examples below.

DESCRIPTION OF PREFERRED EMBODIMENTS

[0010] The packaging article provided herein preferably is in the form of a bottle, which may have any convenient volume and generally is formed by blow moulding. At least a wall and preferably the entire article, is constructed of a linear polyester, preferably PET, prepared by condensation of an aromatic dicarboxylic acid component and a diol component. For the provision of PET, terephthaltic acid and diethylene glycol are condensed.

[0011] The polyester contains at least one oxygen scavenging material, which may be provided as a discrete layer or preferably is uniformly distributed throughout the container wall. The oxygen scavenging material may be any of the materials known to be useful in the art for such purposes, but preferably is a polyester copolymer comprising predominantly polyester segments and an oxygen scavenging amount of polyolefin oligomer segments. Such polyester copolymers are described in detail in US Patent No. 6,083,585, the disclosure of which is incorporated herein by reference. Such materials are available commercially under the trademark AMOSORB.

[0012] The polyester segment of the polyester copolymer usually is the same polyester used to construct the container, preferably PET. The polyolefin oligomer segments are distributed throughout the predominant polyester segments of the copolymer and are present in sufficient quantity in the copolymer to provide the needed oxygen scavenging capacity. The hydrocarbon segments are the only moieties present which have oxygen scavenging propensity and capacity. The polyester copolymer preferably has an oxygen scavenging capacity of at least about 0.4 cc of oxygen per gram of copolymer at a temperature in the range of about 4° to about 60°C, preferably at least 10 cc of oxygen per gram of copolymer and more preferably at least 20 cc per gram.

[0013] The polyolefin segments may be provided by polypropylene, poly(4-methyl)1-pentene, unhydrogenated polybutadiene or mixtures thereof, preferably dihydroxy-terminated unhydrogenated polybutadiene, which may have a molecular weight in the range of about 100 to about 10,000, preferably in the range of about 1000 to about 3000. The polyolefin segments may comprise about 0.5 to about 12 wt% of the polyester copolymer.

[0014] To provide an adequate oxygen absorbing capacity to the container, such polyester copolymer often is employed in amounts of about 4 to 5 wt% of the container wall. By employing the external barrier coating in accordance with the invention, this amount of oxygen scavenging material may be significantly reduced to about 1 wt% and still provide improved performance.

[0015] The external coating of barrier material is applied as a very thin continuous layer, often less than a micron in thickness, at least to the walls of the container and preferably also to the neck and base of a bottle. Depending on the size of the bottle and the nature of the coating, a coating applied to the walls only may be sufficient. The external coating may be applied in any convenient manner, depending on the material used to provide the coating, preferably by spraying. Generally, sufficient material only is used to provide a continuous coating of barrier layer on the desired portion of the bottle so as to minimize the material costs and to

provide transparency to the coating. Each coating may have a thickness of about 0.3 to about 0.5 mil (about 5 to 15 microns).

[0016] The material used to provide the external barrier coating should be a material generally impervious to gaseous flow therethrough, particularly oxygen, and, where the container is to be used for carbonated beverages, also by carbon dioxide. The material utilized to provide the barrier coating may be an epoxy resin, plasma-deposited silica or carbons, vapor-deposited silica or an ester-based UV-curable polymeric material. Any other suitable material which provides a passive barrier to the passage of air and/or carbon dioxide may be employed.

[0017] Preferably, the barrier coating is provided by an epoxy-amine resin. Such barrier materials are described in U.S. Patents Nos. 5,300,541, 5,637,365 and 4,309,367 among others, the ducrosures of which are incorporated herein by reference. Such film-forming epoxy-amine resins are generally formed by reacting a polyamine and a polyepoxide.

[0018] Preferably, the barrier material is provided by an epoxy-amine copolymer constructed as described in the aforementioned U.S. Patent No. 5,637,365. Such materials employ an amine hydrogen to epoxy equivalent cure ratio lower than 1.5 to 1. The amino contents of the cured coating may be less than seven percent with good results being obtainable as low as four percent or lower. The relatively lower amino content of the coating generally has the advantage of less yellowing of the coating over time. Such material are sold by PPG Industries under the trademark BAIROCADE.

[0019] As mentioned above, when the barrier coating is employed in conjunction with a PET constructed of a monolayer of material having an active oxygen scavenger material distributed throughout the walls, then the amount of oxygen scavenger material which is used can be reduced and an improved bottle performance can be achieved. This ability to employ less oxygen scavenger material is advantageous, in terms of cost of materials and has the effect of improving bottle clarity.

[0020] By employing the barrier coating herein in conjunction with the oxygen scavenger material, the overall performance of the container in terms of gas permeability is improved. Both the empty bottle and full bottle shelf-lives are improved. In the case of carbonated beverages, the barrier coating prevents carbon dioxide from exiting the container through the walls, thereby improving the shelf-life for such materials.

[0021] In particular, as may be seen from the data presented in the Examples, the presence of an epoxy-amine polymer coating on bottles constructed of PET having an oxygen scavenger uniformly distributed in the walls generally improves both the barrier to oxygen transmission and oxygen absorbing capacity, as compared to the absence of such coating. While permitting bottles to stand prior to filling reduces the combined effectiveness of the epoxy-amine polymer coating on an oxygen-scavenger containing wall, the total oxygen transmittance can be significantly reduced and the package with the combination is much more effective for bottling all types of beer and other oxygen-sensitive foods and beverages.

EXAMPLES

[0022] The oxygen permeance measurements made in the Example are obtained by a liquid oxygen sensitive indicator method, which represents oxygen ingress into the liquid. The method correlates were with oxidative degradation of a model ascorbic acid solution and with results by trained taste pnaelists.

Example 1:

[0023] This Example illustrates the invention.

[0024] A 34 g PET beer bottle having 1% of an oxygen scavenger dispersed in the walls was provided with an epoxy-amine coating. An improvement in oxygen barrier rate when compared to the absence of the epoxy-amine coating was determined to be 3.8 times.

Example 2:

[0025] This Example illustrates the significant effect of an oxygen scavenger in conjunction with an external barrier layer.

[0026] Polyethylene-terephthalate (PET) bottles were blown from a blend of commercial PET and 1 wt% Amosorb (OFC grade) with 473 ml capacity. Amosorb is a proprietary oxygen scavenging copolymer material supplied by BP chemicals. The copolymer is a copolymer of PET having polybutadiene oligomer segments and is produced as described in the aforementioned USP 6,083,585. The bottles were spray coated on the outside of the bottles with a contiguous outer film of an epoxy-amine resin supplied by PPG Industries under the trademark "BAIROCADE" and produced as described in the aforementioned U.S. Patent No. 5,637,365. The thickness of the layer was about 0.4 mil.

[0027] Control bottles were also prepared in which there was only no modification to the bottle walls, in which only 1% Amosorb was present and in which only the epoxy-amine resin coating was present.

[0028] The bottles were filled with oxygen-sensitive liquid and the total oxygen absorbance by the liquid was determined for a period of time. The results obtained were plotted graphically and appear in Figure 1. As may be seen from the Figure, while both 1% Amosorb and epoxy-amine oxygen resin alone led to a longer period of time over which oxygen was absorbed, the combination of the 1% Amosorb and epoxy-amine resin led to a significant increase in scavenging time with the absorbtion increasing only slowly once steady state conditions had been enhanced.

[0029] The oxygen transmission rate (OTR) was also determined and these results are plotted graphically in Figure 2. While both 1% Amosorb and epoxy-oxygen resin alone reduced the oxygen transmission rate of the bottle when compared to the absence of such materials, the combination leads to a further order of magnitude reduction in the oxygen transmission rate.

<u>Example 3</u>:

[0030] This Example illustrates the synergistic effect of an oxygen scavenger material in conjunction with an external barrier layer.

[0031] The procedure of Example 2 was repeated except that a comparison was made between bottles which were filled immediately after the bottles were made and these which were filled after 5 weeks standing empty ("aged").

[0032] The results obtained for oxygen absorbance of the aged bottles were plotted graphically and appear in Figure 3. These results show the same kind of results as Figure 1 for the unaged bottles. The oxygen transmission rate (OTR) for the aged and unaged ("Time 0") bottles were plotted graphically and appear in Figure 4. These results show that, while the 1% Amosorb containing bottles exhibited a greater OTR in the aged bottles, showing some loss of effectiveness of the Amosorb material, the external epoxy-amine coating significantly reduced the OTR by an order of magnitude.

<u>Example 4</u>:

[0033] This Example describes a study of the effect of Amosorb and PPG on total oxygen absorbance over a four month period.

[0034] Beer in plastic bottles has a finite shelf-life due to oxygen permeation. A four-month period of time usually is considered acceptable. For light-flavoured beer, less oxygen absorbance is tolerable than for stronger-flavoured beer.

[0035] The procedure of Example 2 was repeated except that 0.473 L (16 oz) bottles were prepared, and filled immediately following manufacture or after 5 weeks ("aged"). Bottles were prepared with no alteration to the bottle, 1 wt% Amosorb, 4 wt% Amosorb, epoxy-amine coating and 1% Amosorb plus epoxy-amine coating. The total ppm oxygen absorbed by oxygen-sensitive liquid during a 4 month period was determined and the results are shown graphically in Figure 5.

[0036] As may be seen from the data presented in Figure 5, the total oxygen permeance was reduced below 1 ppm by either using 4% Amosorb or by using 1% Amosorb with epoxy-amine external coating, i.e. below the acceptable levels for any beer.

<u>Example 5</u>

[0037] The Example illustrates the use of a different barrier layer material.

[0038] PCT bottles were blown from a blend of commercial PET and 2 wt% Amosorb with 700 ml capacity. The bottles are coated with silica by high vacuum deposition on the outside of the bottles with a spray-applied polymeric top coat. The coating materials are sold under the tradename BestPET by Krones.

[0039] The bottles were filled with oxygen-sensitive liquid and the total absorbance by the liquid was determined for a period of time and the oxygen transmission rate (OTR) for bottles which has been aged (see Example 3) for 3, 7 and 14 weeks prior to filling. The results obtained are set forth in the following Table I:

TABLE I

Bottles	O_2 ingress (ppm)	OTR (cc/pkg/day)
Aged 3 weeks	0.81	0.0021
Aged 7 weeks	2,07	0.0056
Aged 14 weeks	4.39	0.0153
Control	8.49	0.413

[0040] As may be seen from Table I, significantly decreased oxygen permeance is obtained by the combination of Amosorb and BestPET as compared to the control, although the effect is eroded by bottle aging as the oxygen scavenging capacity of the Amosorb is decreased by the bottles standing empty.

SUMMARY OF DISCLOSURE

[0041] In summary of this disclosure, the present invention provides containers having walls constructed of polyester with an oxygen scavenging material therein and a barrier coating applied thereto to provide an improved performance with respect to gas permeation. Modifications are possible within the scope of the invention.

CLAIMS

What we claim is:

1. A packaging article having at least a wall constructed of a polyester having an oxygen scavenging material therein and having an external barrier to gas flow thereon.

2. The article of claim 1 wherein said oxygen scavenging material is uniformly distributed through the thickness of the wall.

3. The article of claim 2 wherein said oxygen scavenging material is polyester copolymer comprising predominantly polyester segments and an oxygen scavenging amount of polyolefin oligomer segments.

4. The article of claim 3 wherein said copolymer is capable of absorbing at least 0.4 cc of oxygen per gram of copolymer at temperature in the range of about 4° to about 60°C.

5. The article of claim 3 wherein said polyolefin oligomer is selected from the group consisting of polypropylene, poly(4-methyl)1-pentene unhydrogenated polybutadiene, and mixtures thereof.

6. The article of claim 5 wherein the polyolefin segments comprise from about 0.5% to about 12 wt% of the polyester copolymer.

7. The article of claim 1 wherein the external barrier comprises a thin coating of an epoxy-amine resin.

8. The article of claim 8 wherein the epoxy-amine resin has an amine hydrogen to epoxy equivalent cure ratio lower than 1.5 to 1.

9. The article of claim 1 wherein the external barrier coating is a thin coating of silica.

10. The article of claim 1 wherein the external barrier is applied to the whole external surface of the article.

11. The article of claim 1 wherein said polyester is polyethylene-terephthalate.

12. The article of claim 11 wherein said article is a bottle.

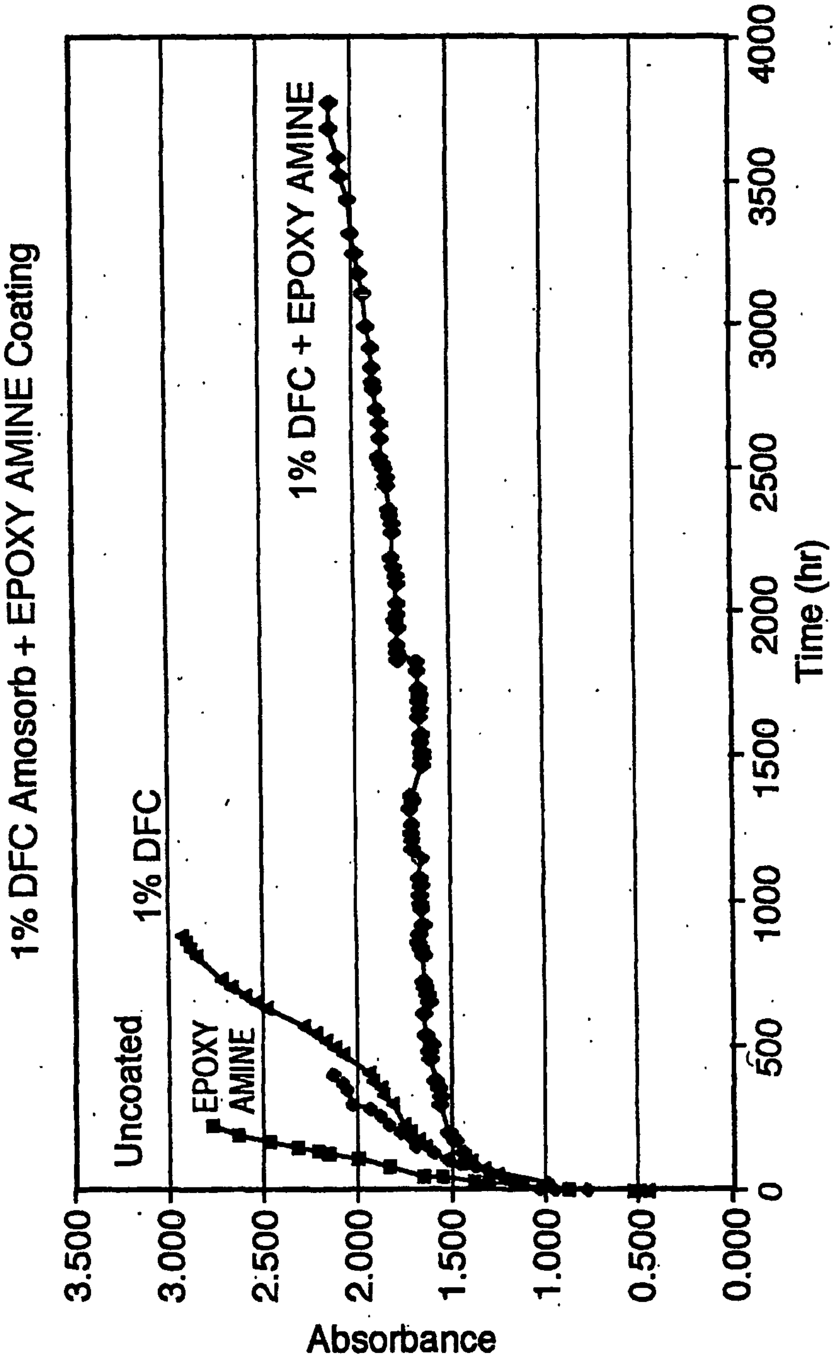
1% DFC Amosorb + EPOXY AMINE Coating
1% DFC
Uncoated
EPOXY AMINE
1% DFC + EPOXY AMINE
3.500
3.000
2.500
2.000
1.500
1.000
0.500
0.000
Absorbance
0
500
1000
1500
2000
2500
3000
3500
4000
Time (hr)

FIG.1

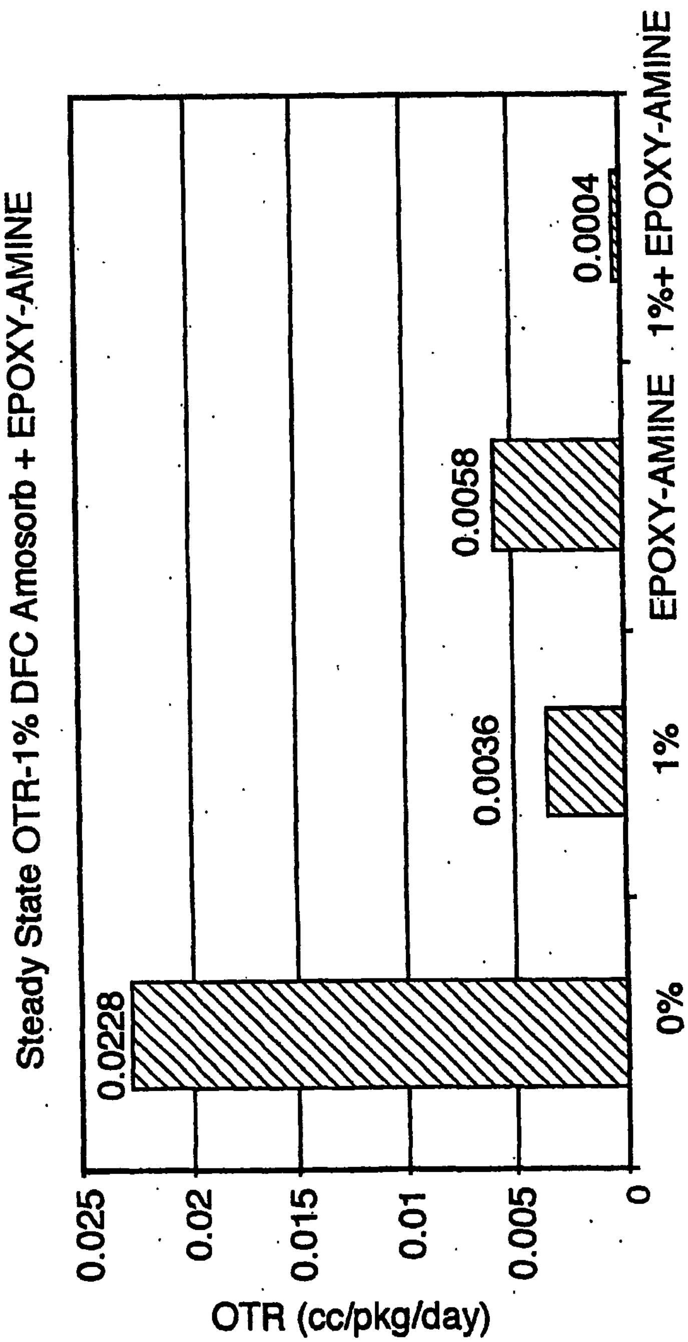
Steady State OTR-1% DFC Amosorb + EPOXY-AMINE
OTR (cc/pkg/day)
0.025
0.02
0.015
0.01
0.005
0
0.0228
0.0036
0.0058
0.0004
0%
1%
EPOXY-AMINE
1%+ EPOXY-AMINE

FIG.2

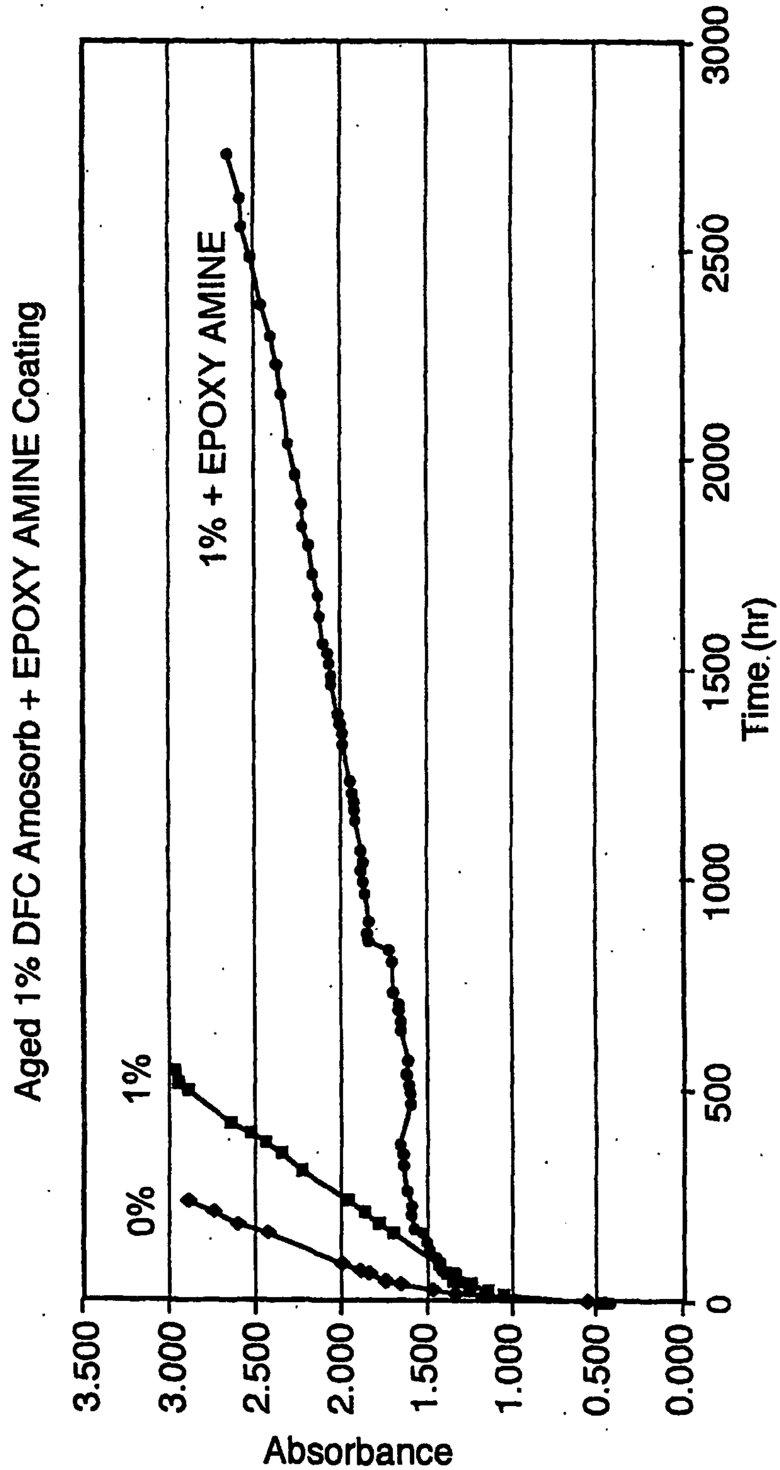
Aged 1% DFC Amosorb + EPOXY AMINE Coating
Absorbance
3.500
3.000
2.500
2.000
1.500
1.000
0.500
0.000
Time (hr)
0
500
1000
1500
2000
2500
3000
0%
1%
1% + EPOXY AMINE

FIG.3

4/15

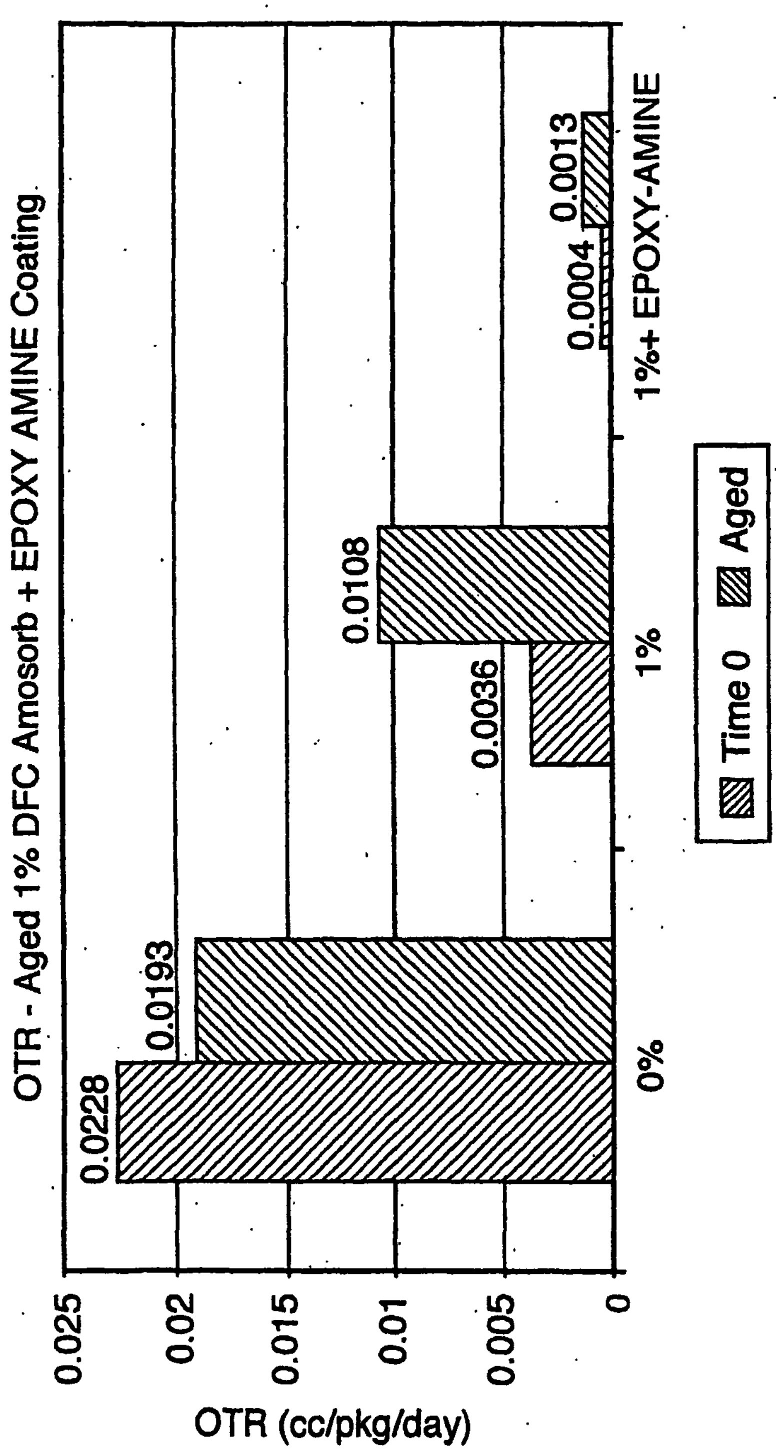
OTR - Aged 1% DFC Amosorb + EPOXY AMINE Coating
OTR (cc/pkg/day)
0.025
0.02
0.015
0.01
0.005
0
0.0228
0.0193
0.0036
0.0108
0.0004
0.0013
0%
1%
1%+ EPOXY-AMINE
Time 0
Aged

FIG.4

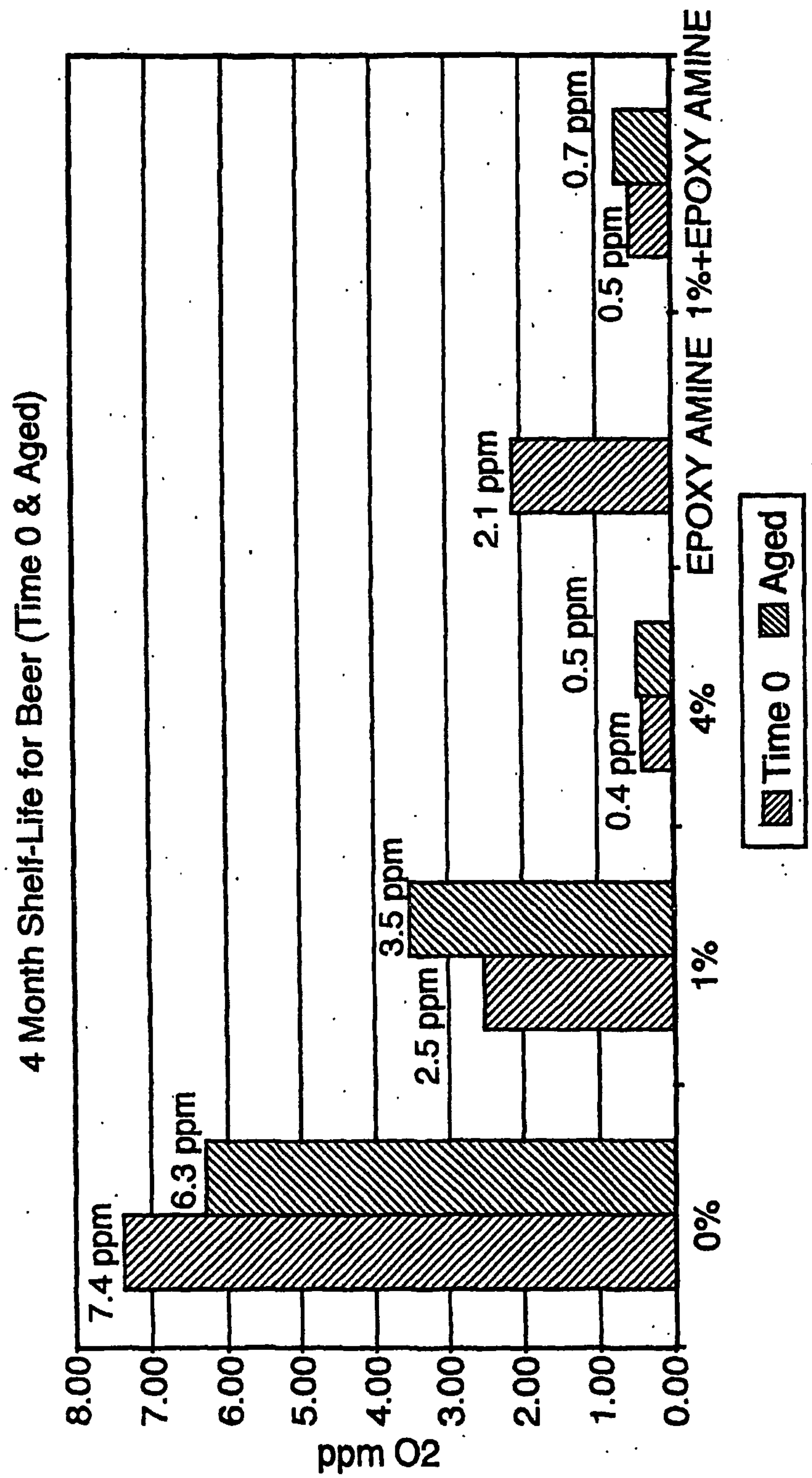
4 Month Shelf-Life for Beer (Time 0 & Aged)
ppm O2
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
7.4 ppm
6.3 ppm
2.5 ppm
3.5 ppm
0.4 ppm
0.5 ppm
2.1 ppm
0.5 ppm
0.7 ppm
0%
1%
4%
EPOXY AMINE
1%+EPOXY AMINE
Time 0
Aged

FIG.5